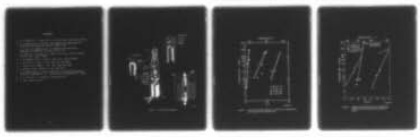
AD-A039 019 STANFORD RESEARCH INST MENLO PARK CALIF PHYSICAL SC--ETC F/G 7/3
THERMAL DECOMPOSITION OF NITROMETHANE AND SOME DINITROALKANES A--ETC(U)
1972 P S DECARLI, D S ROSS, R SHAW, E L LEE N00014-70-C-0190

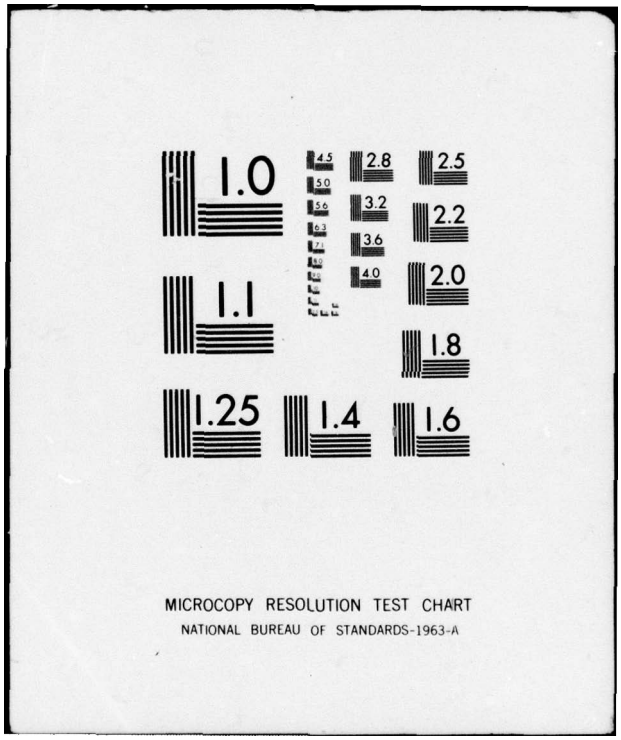
UNCLASSIFIED WSCI-72-10 NL

| OF |
AD
A039019



END

DATE
FILMED
5-77


1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0
5.6
6.3
7.1
8.0
9.0
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD A039019

(1)

(11) 1972 (12) 16 p.

(14) WSCI-72-10

(6)

THERMAL DECOMPOSITION OF NITROMETHANE AND SOME DINITROALKANES AT STATIC HIGH PRESSURES OF 1 TO 50 KBAR,

E. L. Lee and H. D. Stromberg

University of California, Lawrence Livermore Laboratory, Livermore, Calif.*

and

(10) P. S. DeCarli, D. S. Ross, and Robert Shaw,

Physical Sciences Division, Stanford Research Institute, Menlo Park, Calif.†

NRL 1972

FEB 1975 RECEIVED NASA STI FACILITY INPUT BRANCH

DDC RECEIVED MAY 3 1977 A

* Performed under the auspices of the U.S. Atomic Energy Commission.

† Supported by the U.S. Office of Naval Research under Contract No. N00014-70-C-0190

(15)

AU NO.
DDC FILE COPY

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

405 048

1 set of 20 pages (15.00)

ABSTRACT

We have measured the thermal explosion times of nitromethane at 1, 10, and 50 kbar and between 160 and 380°C. At constant pressure, the explosion time decreases as the temperature increases. At constant temperature, the explosion time decreases as the pressure is increased. For a constant explosion time of 10 seconds, at 1 kbar the required temperature is 369°C, at 10 kbar it is 327°C, and at 50 kbar it is 225°C. The increase in decomposition rate with increasing temperature is explainable by Arrhenius-type kinetics. The reasons for the increase in decomposition rate with increasing pressure remain to be determined.

We have also measured the thermal explosion times of some isomeric dinitropropanes at a constant pressure of 10 kbar in the temperature range 130 to 310°C. For a constant thermal explosion time of 20 seconds, the dinitropropanes that do not have a hydrogen atom on the same carbon as the dinitro group require a higher temperature than those that have such a hydrogen. Specifically, the temperatures corresponding to a 20 second explosion time at 10 kbar pressure are 2,2-dinitropropane 269°C; 1,1,1-fluorodinitropropane 242°C; 1,1-dinitropropane 172°C; 1,2-dinitropropane 162°C.

ACCESSION for
NTIS White Section
DDC Buff Section
UNANNOUNCED
JUSTIFICATION
Letter on file
BY
DISTRIBUTION/AVAILABILITY CODES
Dist. AVAIL. and/or SPECIAL
A

C-1824-2

INTRODUCTION

Thermal explosion times play important roles in current theories of the transient detonation processes, shock initiation,[1] and detonation failure.[2] In shock initiation experiments it is not easy to vary shock pressure and shock temperature independently and, furthermore, the p-v-T equations of state in the regions bounded by the Hugoniot are not known. Static high-pressure experiments offer solutions to these problems and give some hope that pressure and temperature effects can be separated. Moreover, the use of isomers that have similar physical properties emphasizes effects due to changes in chemical structure.

EXPERIMENTAL

The LLL apparatus has already been described in detail.[3] The Stanford Research Institute setup uses the same gold reaction vessels, but the heating arrangement has been redesigned in the hope of better temperature control. Accordingly, we have adapted the "Teflon cell" technique[4] to the requirements of the present program. The Teflon cell geometry is shown in Figure 1.

The sample under investigation is loaded into a gold sample container of the double cup type, obtained from the same source as those used by Lee et al. As supplied, the cups do not fit together well enough to form a liquid-tight seal. We have found it necessary to swage the closed end of the larger cup to a slightly smaller diameter. To avoid the possibility of air bubbles in the sample liquid, the container is assembled and sealed while immersed in the liquid. A small lip, similar to a pouring lip, is formed in the outer gold cup. A Chromel-Alumel thermocouple is inserted into the space between the lip and the inner cup, and the lip is then crimped down to hold the thermocouple in place.

The sample container is surrounded by a heater assembly; the sample thermocouple-heater assembly is placed in a silicone oil-filled Teflon cell, and the Teflon cell is placed in a conventional piston-cylinder apparatus. When force is applied to the piston, the sample is subjected to a hydrostatic pressure transmitted by the silicone oil, which also serves as a heat transfer medium. The Teflon cell is a very effective leakproof container at high pressures, and the system has low friction. The pressure in the fluid can be calculated from the force-piston diameter relationship with an accuracy of about 5%. Hanneman and Strong[5] have found the effect

of pressure on the output of Chromel-Alumel thermocouples is negligible, equivalent to an error of less than $1^{o}C$, up to pressures of 30 kbar. On the time scale of interest in the present experiments (time to explosion of 1 sec or more), the temperature difference between the sample and the thermocouple junction should not exceed about $1^{o}C$. We have found no evidence of emf induced in the thermocouple by coupling with ac heating current. We therefore believe that the present apparatus permits measurement of sample temperature with an accuracy of $1^{o}C$.

For these experiments, the thermocouple cold junctions were maintained at the ice point, and the thermocouple output was monitored by a Varian Model G-11A millivolt recorder. Power output to the heater was controlled manually by a variable transformer connected to the primary of a 12-volt filament transformer. A Leeds and Northrup Model 9693 potentiometer was used to calibrate the Varian recorder immediately prior to and immediately following each experimental run.

In a typical run, the Teflon capsule was first pressurized to the desired level, e.g., 10 kbar. In the first several experiments, the temperature was controlled manually, and an initial current of about 8 amp was passed through the heater. When the sample temperature, as indicated by the millivolt recorder, reached the desired level, the heater current was reduced to a level (generally 3 to 4 amp) sufficient to maintain temperature. The temperature was maintained within a fairly narrow range, $\pm 3^{o}C$, by appropriate adjustments of the variable transformer. An abrupt off-scale excursion of the recorder pen marked the time of explosion. The sound of the explosion was well muffled by the pressure vessel; one might describe the sound as roughly equivalent to the sound of a typewriter bar striking the paper.

Under manual control, it was difficult to reduce the heat-up time to less than about 20 sec (heating rate of $15^{o}C$/sec). Accordingly, a simple solid-state controller has been constructed, which permits much shorter heat-up times as well as more accurate control of the test temperature during the run. The controller is now used routinely in all of our static high-pressure runs.

The pressure in the Teflon cell increased by about 5% during the heat-up. We infer from the results of Lee, Sanborn, and Stromberg that our results would not be affected by such minor pressure variations, and we have no current plans for improvement of the pressure system.

RESULTS AND DISCUSSION

Nitromethane

We chose nitromethane for the first series of experiments because it is one of the most studied liquid explosives.[1] The results are in Figure 2. Experiments were made at 10 kbar in both the LLL and SRI apparatus to check for consistency. The results agree within the experimental error, considering the differences in the methods of heating and temperature measurement. The LLL results at 10 and 50 kbar have been previously reported. At constant pressures of 1, 10, or 50 kbar the explosion time decreases as the temperature is increased, in line with previous results[3,6-8] on other explosives at pressures of 1 atmosphere and above. Arrhenius activation energies and A-factors for the heat-releasing chemical reactions can be calculated from the results using thermal explosion theory as developed by Zinn and Mader[6] and by Zinn and Rogers.[7] In this calculation, the explosive in the present experiments may be taken as spherical. The thermal time constant τ is given by $\tau = \rho c_v a^2/\lambda$, where ρ is the density, a is the radius, c_v is the heat capacity at constant volume, and λ is the thermal conductivity. Taking ρ as 1.5 g/cc, c_v as 0.3 cal/(mole deg), a as 0.2 cm, and λ as 0.0005 cal/(deg cm sec) (assumed to be the same as for TNT[6]), then τ = 36 sec. Zinn and Mader[6] showed that $t_{exp}/\tau = F[(E/T_m) - (E/T_1)]$, where t_{exp} is the explosion time at T_1 and T_m is the minimum temperature for thermal explosion to be observed. From the results in Figure 1 at 50 kbar, T_m = 160°C (433°K) and at T_1 = 225°C (498°K), t_{exp} = 10 sec. That is, $t_{exp}/\tau = 10/36 = 0.28$. From Zinn and Mader's calculations at t_{exp}/τ = 0.28, $[(E/T_m) - E/(T_1)]$ (for a sphere) = 6.

$$\therefore \quad \frac{E}{T_m} - \frac{E}{T_1} = 6$$

$$\text{i.e.} \quad E = \frac{6T_mT_1}{T_1 - T_m}$$

$$= \frac{6 \times 498 \times 433}{498 - 433}$$

$$= 20 \text{ kcal/mole.}$$

The Arrhenius A-factor is obtained from the equation[6]

$$T_m = \frac{E}{2.303R \log (\rho aQAE / \lambda RT_m^2 \delta)}$$

where Q is the heat of explosion and δ is 3.32 for a sphere. Taking Q as 1.28 kcal/mole and E as 20 kcal/mole, substitution gives $A = 10^6$ sec^{-1}. That is, the rate constant for the heat-releasing chemical reaction at 50 kbar for nitromethane is given by $k = 10^{6-(20/\theta)}$ sec^{-1}, where θ is 2.3 RT. It is generally recognized that Arrhenius parameters are highly subject to systematic errors, but that the rate constants at a temperature within the experimental range are much more reliable. In our discussion, we will therefore emphasize differences in rate constant, rather than differences in Arrhenius parameters. At the temperature of the experiments, say at 225°C, $\theta = 2.28$, i.e., $k = 10^{-2.8}$ sec^{-1}. This rate constant may be compared with that for C-N bond fission,[9] $k = 10^{15.6-(59/\theta)}$ sec^{-1}. At 225°C, $k = 10^{15.6-(59/2.28)} = 10^{15.6-25.8} = 10^{-10.2}$. That is, the rate of nitromethane decomposition at 50 kbar and at 225°C is $10^{7.4}$ times faster than C-N bond fission.

The Arrhenius parameters calculated for the 1-kbar results, $k = 10^{40-(127/\theta)}$ sec^{-1}, are unusually large and should not be used to extrapolate rates outside the experimental temperature range.

Perhaps the most interesting feature of the nitromethane results is that the explosion times vary with pressure. There are two ways of looking at the results. The range of explosion times is such that there is no common temperature at which explosion times have been measured for all three pressures, namely, 1, 10, and 50 kbar. Thus we cannot make a direct observation of the variation of explosion time with pressure at constant temperature. However, by extrapolating only a little, it is possible to compare the 50-kbar results with those at 10 kbar and to compare the 10-kbar results with those at 1 kbar. At 225°C, at 50 kbar the explosion time is 10 seconds, whereas at 10 kbar, the explosion time is 500 seconds. That is, at 225°C, an increase of a factor of 5 in pressure causes a decrease of 50 in explosion time. Because of the method of deriving chemical reaction rate constants from the explosion times, the difference in rate constant need not be the same as the difference in explosion time. Thus at 50 kbar, the calculated rate constants (in Table 1) differ by a factor of 80, whereas the explosion times differ by a factor of 50. Comparing the 10-kbar results with those of 1 kbar, at 369°C, the explosion times differ by a factor of 5, whereas the rate constants differ by 10.

If the explosion time is kept constant, say at 10 seconds, then the corresponding temperature at 1 kbar is 369°C; at 10 kbar it is 327°C; and at 50 kbar it is 225°C. This constant explosion time approach allows ready comparison of all the pressures to be made. Wenograd[8] used this method to compare his thermal explosion results with the results of impact tests.

Table 1

ARRHENIUS PARAMETERS AND RATE CONSTANTS

FOR NITROMETHANE DECOMPOSITION

	log (A/sec^{-1})	E kcal/mole	11 + log(k/sec^{-1})		
			225°C	327°C	369°C
50-kbar results	6	20	8.2		
10-kbar results	5.3	22	6.3	8.3	8.8
1-kbar results	40	127			7.8
C-N Bond Fission	15.6	59	0.8	5.2	6.4

Either way, it is clear that in this temperature and pressure range increasing the pressure causes a significant increase in rate of decomposition. The reasons for the increase remain to be determined.

Dinitropropanes

Thermal explosion times at 10 kbar are shown in Figure 3 for three isomeric dinitropropanes:

$CH_2(NO_2)CH(NO_2)CH_3$	$CH(NO_2)_2CH_2CH_3$	$CH_3C(NO_2)_2CH_3$
1,2-dinitropropane	1,1-dinitropropane	2,2-dinitropropane
1,2-DNP	1,1-DNP	2,2-DNP

These isomers have similar physical properties and were studied in the hope of shedding light on the chemistry of the thermal decompositions. It is clear from the figure that 1,2-DNP and 1,1-DNP decompose at comparable rates and that both react faster than 2,2-DNP. C-N bond fission is not the rate-determining process, because the C-N bond in 1,2-DNP must be similar to that in nitromethane, namely, 59 kcal/mole, whereas the C-N bond strengths in 1,1-DNP and 2,2-DNP are about 45 kcal/mole.[10] Nor is five-center elimination of HONO the rate-determining process, because HONO elimination requires a β-hydrogen atom, and all three isomers have hydrogen atoms β to the nitro groups. The results suggest that the presence of an α-hydrogen

atom causes an increase in the rate of decomposition. As a test of this hypothesis, we have begun a series of experiments with

$$CF(NO_2)_2CH_2CH_3$$

1,1,1-fluorodinitropropane

1,1,1-FDNP

which has no α-hydrogen atom. Preliminary results shown in Figure 3 indicate that 1,1,1-FDNP decomposes significantly slower than 1,1-DNP.

It is interesting to note that in recent shock initiation experiments,[11] for the same initiating shock pressure in the liquid, 1,1-DNP had a shorter reaction time than 2,2-DNP, and 1,1-DNE had a shorter reaction time than 1,1,1-FDNE. In both cases, the compound that reacted slower had no α-hydrogen atom.

Although there is clear indication that the presence of a hydrogen atom α to the nitro group increases the rate of decomposition, the detailed mechanism is not yet clear.

REFERENCES

1. A. W. Campbell, W. C. Davis, and J. R. Travis, Phys. Fluids 4, 498 (1961).
2. A. N. Dremin and V. S. Trofimov, Tenth Symposium (International) on Detonation, The Combustion Institute, 1965, p. 829.
3. E. L. Lee, R. H. Sanborn, and H. D. Stromberg, Fifth Detonation Symposium, The Combustion Institute, 1970, p. 271.
4. A. Jayaraman, A. R. Hutson, J. H. McFee, A.S. Coriell, and R. G. Maines, Rev. Sci. Inst., 38, 44 (1967).
5. R. E. Hanneman and H. M. Strong, J. Appl. Phys., 36, 523 (1965).
6. J. Zinn and C. L. Mader, J. Appl. Phys., 31, 323 (1960).
7. J. Zinn and R. N. Rogers, J. Phys. Chem., 66, 2646 (1962).
8. J. Wenograd, Trans. Faraday Soc., 57, 1612 (1961).
9. S. W. Benson and H. E. O'Neal, "Kinetic Data on Gas-Phase Unimolecular Reactions," NSRDS-NBS 21, Gov't Printing Office, Washington, D.C. (1970).
10. D. S. Ross and L. W. Piszkiewicz, unpublished work.
11. R. Shaw, unpublished work.

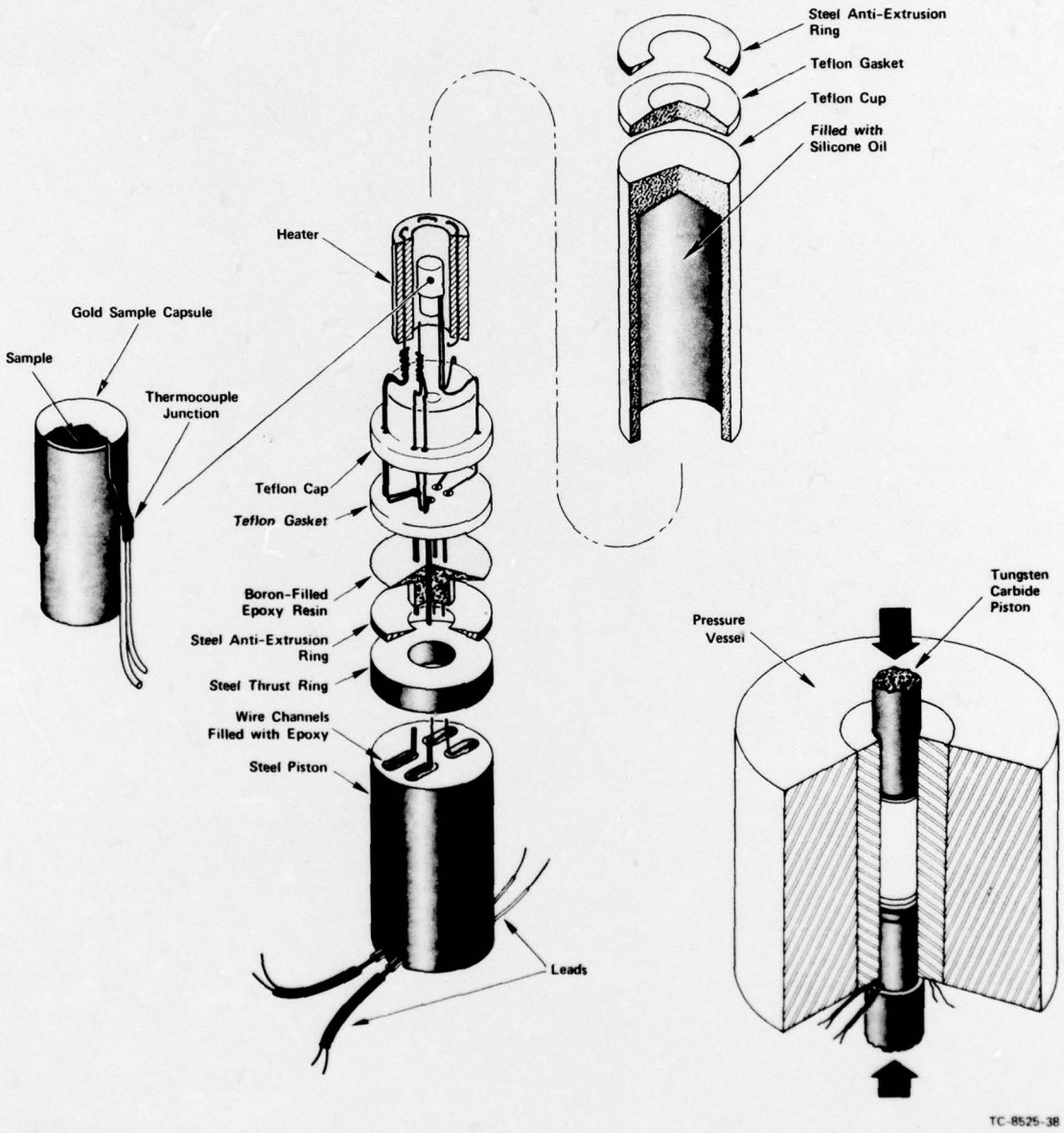


FIGURE 1 TEFLON CELL GEOMETRY

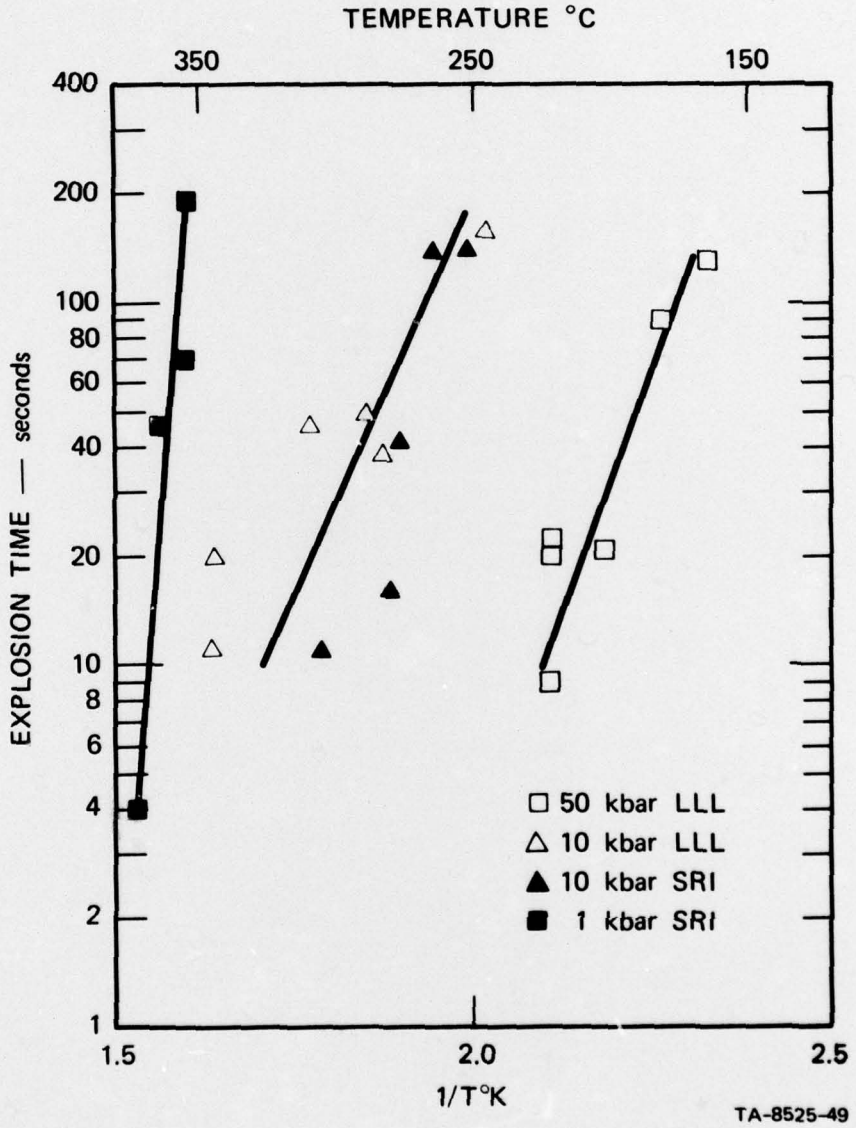


FIGURE 2 THERMAL EXPLOSION TIMES AS A FUNCTION OF TEMPERATURE AND PRESSURE FOR NITROMETHANE

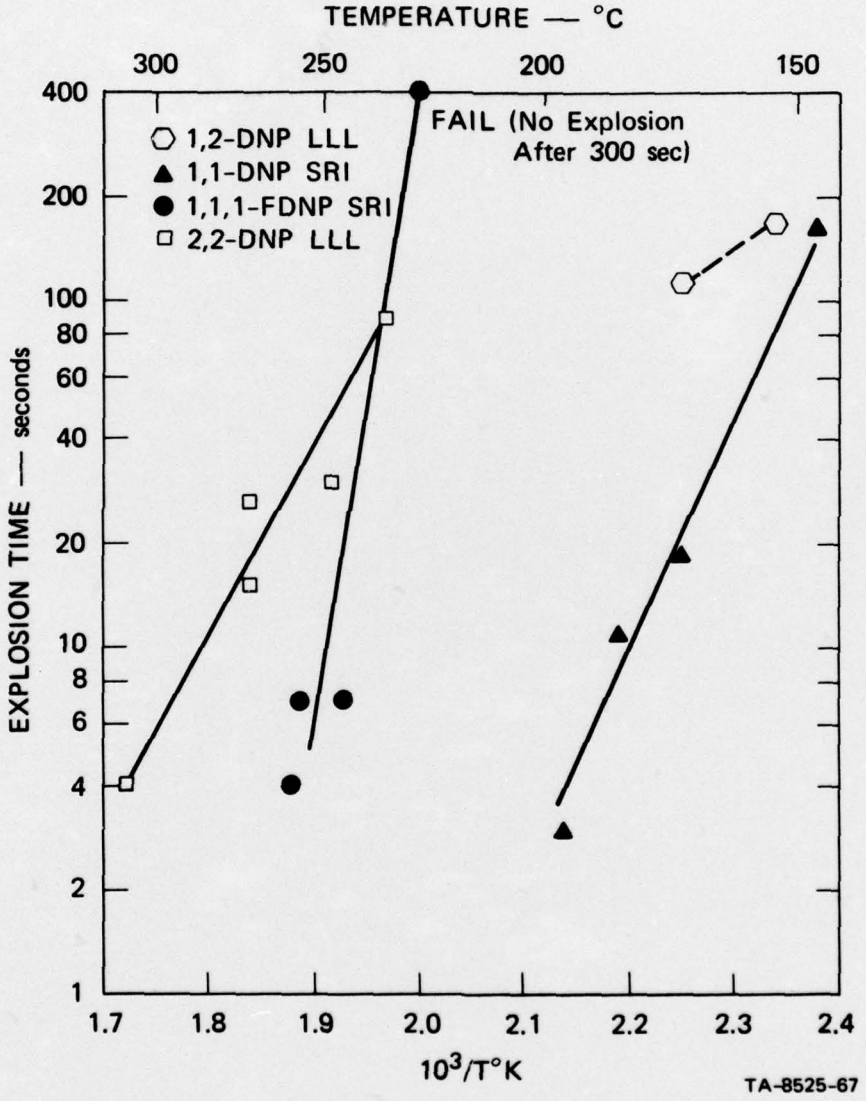


FIGURE 3 THERMAL EXPLOSION TIMES AS A FUNCTION OF TEMPERATURE FOR SOME DINITROALKANES AT 10 kbar